



# PATENT SPECIFICATION

707,994

Date of Application and filing Complete Specification: Feb. 8, 1951.

No. 3146/51.

Application made in Germany on Feb. 13, 1950.

Application made in Germany on Feb. 23, 1950.

Complete Specification Published: April 28, 1954.

Index at acceptance:—Class 2(3), C3C10.

## COMPLETE SPECIFICATION

### Process for the Neutralization of Sulphonic Acids

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holteln, Germany, a German joint-stock Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to improvements in the neutralization of sulphonic acids.

Alkyl, aryl or alkyl-aryl sulphonic acids are neutralized with alkalis either intermittently or in continuous manner for the manufacture of sulphonates.

A very common method of carrying out the neutralization has been to dissolve the sulphonic acid in water and to treat the solution so formed with an aqueous solution of an alkali-metal hydroxide. After neutralization, the water added together with that formed during the reaction is removed by evaporation or atomization in known manner. One particular mode of effecting the neutralization by this method has been to use a rapidly rotating plate provided with jets, the sulphonic acid and the aqueous alkali solution being poured on to the rotating plate. The rotating plate scatters the mixture of the reactants in fine particles into a reaction chamber into which hot air is simultaneously blown. The immediate end product may constitute a dried washing agent or detergent. These well-known methods are unsatisfactory as relatively large quantities of water have to be evaporated. Furthermore, such methods do not permit the aqueous alkali-metal hydroxide to be replaced by an aqueous solution of an alkali-metal carbonate since the use of the latter leads to the formation of an excessive amount of foam.

One proposal which has been made to avoid the formation of foam in the neutralization of sulphonated products with carbonates or bicarbonates consists in effecting the neutralization in the absence of a diluent other than water formed in the neutralization or added in such a proportion that the mixture

will contain at every stage of the neutralization a proportion of water, less than 40% and less than a proportion which causes foam- 50 ing of the mass.

It has now been found that sulphonic acids, particularly such as will yield detergents upon neutralization, may be neutralized in an advantageous manner by intimately admixing 55 the acids with a dry alkali-metal carbonate and/or a dry alkali-metal hydroxide, the admixing being effected in a zone into which the reactants are sprayed in finely divided form. 60

According to the invention therefore, a process for the neutralization of a sulphonic acid comprises intimately admixing the acid with a dry alkali-metal hydroxide and/or carbonate by spraying the reactants simultaneously and in finely-divided form into a reaction zone. 65

A small quantity of water may be used with advantage to accelerate the reaction and the quantity of water so used need not exceed 10–15% by weight of the sulphonic acid. The water is either contained in or admixed with the sulphonic acid prior to admixture of the acid with the dry carbonate or hydroxide, or the water is introduced separately into the reaction zone during the neutralization. Alternatively, part of the water may be admixed with the acid whilst the remainder of the water is introduced separately into the reaction zone during the neutralization. 70 75 80

If the state of division of the reactants is sufficiently fine, the neutralization may be completed in a relatively short time. The quantity of alkali-metal carbonate and/or hydroxide used should be at least sufficient to neutralize the sulphonic acid. Where an alkali-metal carbonate is used in the process according to the invention, the evolution of carbon dioxide will not lead to any difficulties. 85

The spraying or atomization of the liquid sulphonic acid can be effected in known manner, for example through nozzles or on rapidly rotating discs. The fine distribution of the dry alkali-metal carbonates or 90

hydroxides can also be effected by means of a nozzle, in which case the required amount of the completely dry and finely pulverized alkali-metal compound is introduced into the reaction zone by means of a gas, such as air, under pressure. The sprayed or atomized stream of sulphonic acid is directed towards the stream of the finely divided alkali-metal carbonate or hydroxide so that an intimate contacting or admixture of the two finely dispersed reactants is obtained. A mixture of this kind is fairly easily obtained by a suitable arrangement of the spray nozzles or other dispersion means. The reactants may with advantage be sprayed into the reaction zone through the same nozzle.

By controlling the amount of air used for injecting the dry, pulverized alkali-metal carbonate or hydroxide, as well as by blowing additional amounts of air into the reaction zone, the rate of removal of the heat generated in the reaction can be easily regulated so that the reaction temperature is kept below a determined upper limit.

Various types of apparatus may be used for carrying out the process according to the invention, sufficient space for intermixing the reactants being provided so that a sufficiently long path is available for the sprayed material before it is prevented from further conversion, for example on the walls of the reaction vessel.

The process according to the invention may, for example be carried out in vertical towers in which the reactants are sprayed from the top towards the bottom. The spraying means for the sulphonic acids and for the pulverized, dry alkali-metal carbonates or hydroxides, or the single spray nozzle for both media, are provided at a suitable position in the upper part of the tower. Thorough distribution of the reactants can also be accomplished in such manner that the spray is directed from the bottom towards the top of the tower. In this way, the sprayed material, which finally collects at the bottom of the tower, passes through almost twice the distance and, furthermore, has a longer residence time in the free space when falling than when the spraying is done from the top toward the bottom. The residence time of the sprayed product can be further prolonged by blowing air tangentially into the tower at several places, which blowing will produce a rotary motion of the sprayed material.

The sprayed material, which collects at the bottom of the tower, is a firm foamy mass the reaction of which is not complete. The mass is removed from the tower, for example with scrapers, and the removal may be continuous or intermittent. From 30 to 120 minutes are required for the mass to be completely neutralized. The mass may remain in the tower for the requisite period or it may

be removed from the tower, for example by a conveyor belt, as it reaches the bottom and may then be stored for a period sufficient for completion of the neutralization. As neutralization proceeds, the product becomes firmer and it can be homogenized by rollers, and can if necessary be treated with hot air in order to dry it completely. When using suitably placed spray nozzles for the reactants, the neutralization of the sulphonic acids can be carried out without any, or only a small addition, of water, so that no great amount of energy is needed for evaporation of the water. Furthermore, a high output with simple apparatus and end products which are completely neutralized, are readily obtained.

The invention is illustrated by the following examples:

#### EXAMPLE 1.

20 kilograms per hour of a sulphonic acid, which was produced by sulphonating a mono-alkyl-benzene the alkyl chain of which contained 10 carbon atoms, was sprayed from the bottom towards the top of a tower 4 metres in height and 1.5 metres in diameter, by means of a spray nozzle placed in the lower part of the tower. The sulphonic acid had been previously diluted with 8% of water and contained 1.84 kilograms of sulphuric acid. The atomization was effected by means of a current of air into which 5.6 kilograms of finely pulverized and anhydrous sodium carbonate (96%  $\text{Na}_2\text{CO}_3$ ) were injected per hour. The pulverized material collected at the bottom of the tower and was continuously removed by means of a scraper. After storage for one hour, it was homogenized by means of rollers and then completely dried by a hot air blower. The finished product was substantially pure white in colour, contained 15% of inorganic salts and 85% of sodium sulphonate, and its reaction was neutral.

#### EXAMPLE 2.

A mono-alkyl-benzene fraction was obtained by distillation of the mixture obtained upon the alkylation of benzene with a chlorinated  $\text{C}_{12}$  petroleum fraction. Aromatic hydrocarbons had been removed from the  $\text{C}_{12}$  petroleum fraction prior to chlorination and the fraction subjected to chlorination had a content of 75% of aliphatic compounds and of 25% of naphthenic compounds. The mono-alkyl benzene fraction was sulphonated with concentrated sulphuric acid resulting in a reaction product which consisted of 86.7% by weight of sulphonic acid, 9.3% by weight of sulphuric acid and 4.0% by weight of water. This sulphonation mixture was sprayed downwardly from the top of a tower 4 metres in height and 2 metres in diameter, by means of a spray nozzle placed in the upper part of the tower. The atomization was effected by means of an air current into which 4.2 kilograms of very finely pulverized anhydrous sodium carbonate was injected per hour. The

sprayed material collected at the bottom of the tower. After storage for 2 hours, neutralization was found to be complete. The salt was removed and completely dried with hot air having a temperature of 80° C. The neutralized product consisted of 84% of sodium sulphonate and 16% of inorganic salts.

#### EXAMPLE 3.

10 A sulphonation mixture obtained by sulphonating a mono-alkyl-benzene having 9 carbon atoms in its alkyl side chain and which, after the addition of water, consisted of 76.2% by weight of sulphonic acid, 7.5%  
15 by weight of sulphuric acid and 16.3% by weight of water, was sprayed at a rate of 8 kilograms per hour through a nozzle placed in the upper part of a tower 4 metres in height and 2 metres in diameter. The spraying or atomization of the sulphonation mixture was effected by means of a current of air charged with powdered, anhydrous sodium carbonate, 2 kilograms of the carbonate being injected per hour. In the lower part of the tower 40 m<sup>3</sup> per hour of air heated to 50° C. were simultaneously blown in tangentially. The reaction product collected at the bottom of the tower. After a residence time of 45 minutes, the reaction product was completely  
20 neutral and it was removed from the tower. It contained 81% of sodium sulphonate, 13% of inorganic salts and 6% of water. By treating it with hot air, it was readily and completely dried.

#### EXAMPLE 4.

35 10 kilograms per hour of a sulphonation mixture, produced by sulphonating a mono-alkyl-benzene having 12 carbon atoms in its alkyl side chain and consisting of 90% by weight of sulphonic acid, 7% by weight of sulphuric acid and 3% by weight of water, was heated to 40° C. and sprayed through a nozzle placed in the upper part of a tower 4 metres in height and 2 metres in diameter.  
40 The spraying or atomization of the sulphonation mixture was effected by means of a current of air charged with very finely pulverized anhydrous sodium carbonate, the carbonate being injected into the tower at the rate of 2.7 kilograms per hour. Through a second nozzle placed directly adjacent to the first nozzle, 1 kilogram per hour of water

was simultaneously sprayed into the tower. 40 m<sup>3</sup> of air heated to 40° C. were also simultaneously blown tangentially into the lower part of the tower. The reaction product collected at the bottom of the tower and after 1 hour it was completely neutral. The reaction product was continuously removed from the tower at such a rate as to give the reactants a residence time of approximately one hour in the tower, the reaction product being thereafter completely dried by a hot air blower. The product contained 86.5% by weight of sodium sulphonate and 13.5% by weight of inorganic salts.

What we claim is:—

1. A process for the neutralization of a sulphonic acid, which comprises intimately admixing the acid with a dry carbonate and/or hydroxide of an alkali-metal by spraying the reactants simultaneously and in finely divided form into a reaction zone.

2. A process according to claim 1, in which the neutralization is effected in the presence of a quantity of water, not substantially in excess of 15% by weight of the acid.

3. A process according to claim 2, in which the water is introduced into the reaction zone together with the acid.

4. A process according to claim 2 or claim 3, in which part of the water is introduced into the reaction zone separately from the reactants.

5. A process according to any one of the preceding claims, in which the neutralized acid is completely dried.

6. A process according to any one of the preceding claims, in which a hot gas is blown into the lower part of the reaction zone.

7. A process according to any one of the preceding claims, in which the reactants are sprayed upwardly into the reaction zone.

8. A process for the neutralization of a sulphonic acid, substantially as hereinbefore described with reference to any of Examples 1 to 4.

9. A neutralized sulphonic acid whenever prepared by the process of any preceding claim.

EDWARD EVANS & CO.,

14—18, High Holborn, London, W.C.1,  
Agents for the Applicants.